# Mechanistic Investigations on *N*-Halosulphonamides. Kinetics of Oxidation of Thiocarbonohydrazide in the Free and Metal-bound States and Diethylidene Thiocarbonohydrazide, in Aqueous and Partially Aqueous Media

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The kinetics of oxidation of thiocarbonohydrazide (TCH) in the free and Zn(i)-bound states and its hydrazone, by *N*-chlorobenzenesulphonamide (chloroamine-B) in aqueous perchloric acid and by *N*,*N*-dichlorobenzenesulphonamide (dichloramine-B) in water-methanol (1:1, v/v) in the presence of perchloric acid, have been investigated. Oxidation by both chloramine-B and dichloramine-B shows first-order kinetics in [oxidant] and fractional order in [substrate]. The rates of reactions are independent of [H<sup>+</sup>]. Addition of the reduced product of the oxidant (benzenesulphonamide) or a variation in ionic strength of the reaction medium has no significant effect on the rate of oxidation, in all cases. However, a decrease in the relative permittivity of the medium, effected by changing the solvent composition with methanol, decreases the rate. Both the Michaelis–Menten type and two-pathway mechanisms are discussed in order to explain the observed results. The rate-limiting steps have been identified and the rate coefficients of these steps calculated at different temperatures by varying the substrate concentrations at each temperature. The latter constants have been used to compute the activation parameters from the Arrhenius plots. The metal complexation of thiocarbonohydrazide has little effect either on the rate of oxidation or kinetic order, while conversion to its hydrazone enhances the rate of oxidations with both the oxidants.

The chemistry of S–N donor ligands such as thiosemicarbazide and its homologues and derivatives is of interest due to their synthetic and analytical applications and biological activity.<sup>1-5</sup> They are good metal chelating agents and find applications in the characterisation of several organic compounds. They are potential pesticides and fungicides and are active against influenza, protozoa, smallpox, and certain kinds of tumour.

Thiocarbonohydrazide  $(H_2NHNCSNHNH_2)$  is a member of the structural sequence thiourea, thiosemicarbazide, and thiocarbonohydrazide and has close links with thiocarbamic and thiocarbazoic acids as well as with aminoguanidines.<sup>2</sup> The chemical behaviour of thiocarbonohydrazide is similar to its keto-analogue carbohydrazide. Thiocarbonohydrazides possess anticarcinogenic and antibacterial properties. The parent compound exhibits a toxicity towards the housefly comparable to that of DDT. It also shows fungicidal properties and has been tested against different species. Although it has been extensively used as a metal chelating agent,  $1^{-3}$  there are no reports on the mechanistic aspects of its reactions in solution. As a part of our mechanistic investigations on reactions of biologically active substrates in the liquid phase, we now report the kinetics of oxidation of thiocarbonohydrazide in the free and metal-bound states and its hydrazone, by N-chlorobenzenesulphonamide (chloramine-B) in aqueous perchloric acid and by N,Ndichlorobenzenesulphonamide in water-methanol (1:1, v/v) in the presence of perchloric acid.

#### Experimental

Materials and Methods.—Chloramine-B (CAB, sodium N-chlorobenzenesulphonamide) was prepared by the partial chlorination of benzenesulphonamide in aq. NaOH (4 mol

dm<sup>-3</sup>).<sup>6</sup> Dichloramine-B (DCB, N,N-dichlorobenzenesulphonamide) was obtained by the chlorination of chloramine-B<sup>7</sup> in aqueous solution. The purity of the oxidants was checked by i.r. spectroscopy and estimation of the amount of active chlorine present. Stock solutions (*ca.* 0.05 mol dm<sup>-3</sup>) of chloramine-B in doubly distilled water and dichloramine-B in methanol were prepared, standardised, and stored in darkcoloured bottles.

Thiocarbonohydrizide was prepared by refluxing a mixture of carbon disulphide and hydrazine hydrate at 90 °C for 1 h. The colourless crystals which separated out were recrystallised from water (m.p. 168 °C, decomp.). Thiocarbonohydrazide was characterized by i.r. spectroscopy and sulphur estimation. The complex bis(thiocarbonohydrazide) zinc(II) chloride was obtained by mixing warm solutions of zinc chloride in dimethyl-formamide (DMF)-water (5:1, v/v) and thiocarbonohydrazide in DMF, in a *ca.* 1:2 mole ratio. The colourless crystals of the metal complex separated out when the solution was allowed to stand for >1 h, and were filtered and washed with hydrochloric acid (0.1 mol dm<sup>-3</sup>) and then dried *in vacuo* over P<sub>2</sub>O<sub>5</sub>.

The hydrazone diethylidine thiocarbonohydrazide was prepared <sup>8</sup> by adding a 50% excess of acetaldehyde in ethanol to a solution of thiocarbonohydrazide in acetic acid (1 mol dm<sup>-3</sup>) and refluxing the resulting mixture for 1 h. The pale yellow crystals obtained were recrystallised from DMF (m.p. 245 °C). The hydrazone was further characterised by i.r. spectroscopy and sulphur estimation.

The stock solutions (ca. 0.05 mol dm<sup>-3</sup>) of thiocarbonohydrazide, its metal complex, and hydrazone were prepared in aqueous perchloric acid (0.1 mol dm<sup>-3</sup>) because their aqueous solutions were unstable and decomposed when left to stand. In aqueous perchloric acid the solutions were stable for several days. The ionic strength of the medium was

			$\kappa_{\rm obs}/10^{-4}{\rm s}^{-1}$						
[ovidant] /	dant] / [substrate] #/ [HCIO]/		тсн		Complex		Hydrazone		
$10^{-3} \text{ mol dm}^{-3} 10^{-2} \text{ mol dm}^{-3} 10^{-2} \text{ mol dm}^{-3} 10^{-2} \text{ mol dm}^{-3}$			САВ	DCB	САВ	DCB	САВ	DCB	
Effect of varyi	ng [oxidant]。								
0.5	2.0	5.0	23.3	14.1	29.8	8.7	35.7	16.4	
1.0	2.0	5.0	23.4	14.2	28.4	8.8	35.7	16.2	
2.0	2.0	5.0	23.1	14.3	28.4	8.2	35.8	16.0	
3.0	2.0	5.0			27.6	8.5	35.5	16.2	
5.0	2.0	5.0	23.5	14.6					
Effect of varying	ng [substrate]	)							
1.0	0.5	5.0	7.9	4.2	19.1	4.4	24.2	9.5	
1.0	1.0	5.0	13.6	6.9	28.4	8.8	35.7	16.2	
1.0	2.0	5.0	23.4	14.2	47.9	18.2	53.0	23.3	
1.0	3.0	5.0		19.1		27.3		35.4	
1.0	4.0	5.0	41.9						
Effect of varying	ng [HClO₄]								
1.0	2.0	2.0	23.0	14.2	28.8	9.3	35.7	16.0	
1.0	2.0	5.0	23.4	14.3	28.4	8.8	35.7	16.2	
1.0	2.0	10.0	23.4	14.6	28.4	8.6	35.5	16.3	
1.0	2.0	20.0	23.4	14.2		8.7			
$0^2$ [complex] <sub>o</sub> =	10 <sup>2</sup> [hydrazon	$ne]_o = 1.0 mol dm$	n <sup>-3</sup> , while vary	ing oxidant and	HClO <sub>4</sub> concen	trations.			

**Table 1.** Pseudo-first-order rate constants for the oxidation of thiocarbonohydrazide (TCH) and its metal complex and hydrazone, by chloramine-B (CAB) in aqueous perchloric acid and dichloramine-B (DCB) in water-methanol (1:1, v/v) at 293 K  $(I = 0.30 \text{ mol } dm^{-3})$ .

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maintained at 0.3 mol  $dm^{-3}$  using a concentrated aqueous solution of sodium perchlorate (Merck). All other reagents used were of accepted grades of purity.

Kinetic Measurements.—The reactions were carried out in glass-stoppered Pyrex boiling tubes under pseudo-first-order conditions with [substrate] (TCH or its metal complex or hydrazone)  $\geq$  [oxidant] (5–40-fold excess). The reactions were initiated by the rapid addition of the requisite amount of oxidant solution, thermally pre-equilibrated at the desired temperature, to solutions containing known amounts of the substrate, perchloric acid, sodium perchlorate, and water [and methanol to maintain the 1:1 (v/v) solvent composition], thermostatted at the same temperature. The progress of the reaction was monitored for at least two half-lives by the iodometric estimation of unchanged oxidants at regular time intervals. The pseudo-first-order rate constants ( $k_{obs}$ ) were computed by graphical methods and the values were reproducible within  $\pm 3\%$  error.

Stoicheiometry and Product Analysis.—The stoicheiometries of TCH–oxidant reactions in the free and metal-bound states and of hydrazone–oxidant reactions were determined by allowing the reactions to go to completion at 303 K at different [HClO<sub>4</sub>] (0.02–0.20 mol dm<sup>-3</sup>) and [substrate]/[oxidant] ratios. The presence of sulphate and carbon dioxide in the reaction products were detected by standard tests,<sup>9,10</sup> and sulphate was estimated gravimetrically.<sup>11</sup> The yields were 94  $\pm$  4%. Benzenesulphonamide (BSA), the reduced product of

## Results

The kinetics of oxidation of thiocarbonohydrazide in the free and Zn(II)-bound states and its hydrazone, by chloramine-B in aqueous perchloric acid and by dichloroamine-B in watermethanol (1:1, v/v) in the presence of perchloric acid, were studied under various reaction conditions. The results are shown in Tables 1-3 and the Figure. At fixed [substrate] (a several-fold excess over oxidant concentration) and  $[HClO_4]$ , the plots of log [oxidant] versus time were linear at least for two half lives, for all the substrates with both the oxidants (Figure). The pseudo-first-order rate constants  $(k_{obs})$  computed from the first-order plots were unaffected by the changes in [oxidant] (Tables 1-3), showing first-order kinetics with respect to [oxidant] in all cases. At constant [oxidant] and [HClO<sub>4</sub>], the rates increased with increasing [TCH], [complex], or [hydrazone]. The plots of log  $k_{obs}$  versus log [TCH], log [complex], or log [hydrazone] were linear with slopes less than one in all cases (Table 3). The plots of either  $k_{obs}$  versus [TCH], [complex], or [hydrazone] or the double reciprocal plots were linear (Figure). The metal complexation of the ligand TCH had little effect either on the rate of oxidation or kinetic order. Conversion into the hydrazone, however, enhanced the rate with both of the oxidants (Tables 1-3).

the oxidants, was detected by t.l.c.<sup>12</sup> using diethyl ether-

chloroform-butanol (2:2:1, v/v) as solvent and iodine as

detecting reagent ( $R_F = 0.88$ ). The equations in Scheme 1 give the observed stoicheiometries per mole of (a) TCH (in the free

and metal-bound state) and (b) its hydrazone.

(a) 
$$H_2NHNCSNHNH_2 + 8PhSO_2NCINa + 6H_2O \longrightarrow 8PhSO_2NH_2 + SO_4^{2^-} + 2N_2 + CO_2 + 8CI^- + 2H^+ + 8Na^+ (4PhSO_2NCl_2)$$
 (8H<sup>+</sup>)

(b) MeCH=NNHCSNNH=CHCH<sub>3</sub> + 
$$8PhSO_2NCINa + 8H_2O - (4PhSO_2NCI_2)$$

$$\begin{array}{l} 8 PhSO_2NH_2 + 2MeCHO + SO_4{}^{2-} + 2N_2 + CO_2 + 8Cl^- + 2H^+ + 8Na^+ \\ (4PhSO_2NH_2) \end{array} \tag{8}$$

Scheme 1.



**Figure.** (A) Plots of  $k_{obs}$  versus [substrate]; a, CAB; b, DCB; 1, TCH; 2, Complex; 3, hydrazone. (B) Plots of  $1/k_{obs}$  versus 1/[substrate]; c, CAB; d, DCB; 1, TCH; 2, Complex, 3, hydrazone.  $10^3$ [oxidant]<sub>o</sub> = 20[HClO<sub>4</sub>] = 1.0 mol dm<sup>-3</sup>, I = 0.3 mol dm<sup>-3</sup>, T = 293 K.

The rates were unaffected by a variation of  $[HClO_4]$  at constant [oxidant] and [substrate], in all cases. Addition of the reduced product of the oxidant (benzenesulphonamide) or a variation in the ionic strength of the medium had no significant effect on the rate of oxidation for all the substrates. A decrease in relative permittivity ( $\varepsilon_r$ ) of the medium, effected by changing the solvent composition with methanol, decreased the rate of all oxidations.

The substrate concentration was varied at different temperatures and the coefficients of the rate-controlling steps were evaluated as described earlier. These constants were used to calculate the activation parameters from the Arrhenius plot (Table 3).

#### Discussion

Chloramine-B (PhSO<sub>2</sub>NClNa) and dichloramine-B (PhSO<sub>2</sub>-NCl<sub>2</sub>), like chloramine-T, dichloramine-T, and bromamine-B, furnish different reactive species in aqueous or partially aqueous solutions depending upon the pH of the medium.<sup>13–18</sup> The

**Table 2.** Kinetic and thermodynamic parameters for oxidations of thiocarbonohydrazide and its metal complex and hydrazone, by chloramine-B (CAB) in aqueous perchloric acid and dichloramine-B in water-methanol (1:1, v/v).

Observed	TCH 1.0 0.8 0 1.0 0.8 0		7p(TCH).Cl.		Hydrazone			
[CAB] [TCH] [H <sup>+</sup> ] [DCB] [TCH] [H <sup>+</sup> ]			1.0 0.0 0 1.0 0.8 0	) 5 3 8	1.0 0.5 0 1.0 0.7 0			
Param- eters	Set I <sup>a</sup>	Set II <sup>b</sup>	Set I <sup>a</sup>	Set II <sup>b</sup>	Set I <sup>a</sup>	Set II <sup>b</sup>		
	Chloramine-B oxidations							
$E_{\rm a}/{\rm kJ}$	122.2	83.3	61.5	38.3	38.3	37.4		
og A	19.7	12.8	8.92	5.02	4,79	4.94		
$\Delta H^{\ddagger}/kJ$	103.0	80.4	54.7	36.7	34.9	34.04		
$\Delta S^{\ddagger}/J K$	68.6	- 10.5	-97.6	-152.5	- 144.0	-161.0		
$\Delta G^{\ddagger}/kJ$ mol <sup>-1</sup>	82.9	83.4	83.3	81.4	83.1	81.2		
	Dichloramine-B oxidations							
$E_{a}/kJ$ mol <sup>-1</sup>	27.18	34.6	23.9	58.2	34.3	49.2		
og A	7.06	3.95	2.2	8.31	3.92	6.74		
$\Delta H^{\ddagger}/kJ$ mol <sup>-1</sup>	24.12	34.75	20.08	57.4	32.35	41.2		
$\Delta S^{\ddagger}/J K$	- 207.9	- 169.19	- 190.80	-87.9	- 175.55	-142.2		
$\Delta G^{\ddagger}/ \text{kJ}$ mol <sup>-1</sup>	85.04	84.32	84.50	83.2	83.78	82.9		

<sup>a</sup> Calculated using  $k_2$  values at different temperatures; see equation (3) and text. <sup>b</sup> Calculated using  $k_3$  values at different temperatures; see equation (6) and text.

following equilibria exist in the aqueous or partially aqueous solutions of chloramine-B and dichloramine-B (Scheme 2).

 $PhSO_2NCI^{-} + Na^{+}$   $PhSO_2NCI^{-} + H^{+} \Longrightarrow PhSO_2NHCI$   $2PhSO_2NHCI \Longrightarrow PhSO_2NCl_{2} + PhSO_2NH_{2}$   $PhSO_2NCl_{2} + H_2O \Longrightarrow PhSO_2NHCI + HOCI$   $PhSO_2NHCI + H_2O \Longrightarrow PhSO_2NH_{2} + HOCI$   $PhSO_2NHCI + H^{+} \rightleftharpoons (PhSO_2NH_2CI)^{+}$   $PhSO_2NCl_{2} + H^{+} \rightleftharpoons (PhSO_2NHCl_{2})^{+}$   $HOCI + H^{+} \rightleftharpoons (H_2OCI)^{+}$   $(PhSO_2NH_2CI)^{+} + H_2O \Longrightarrow PhSO_2NH_{2} + (H_2OCI)^{+}$ 

#### Scheme 2.

Therefore, the probable reactive species in aqueous acid or partially aqueous solutions of chloramine-B and dichloramine-B are  $PhSO_2NHCl$ ,  $PhSO_2NCl_2$ , and HOCl at low  $[HClO_4]$  and  $(PhSO_2NH_2Cl)^+$ ,  $(PhSO_2NHCl_2)^+$ , and  $(H_2OCl)^+$  at high  $[HClO_4]$ .

**Table 3.** Calculated equilibrium constants and rate coefficients of the rate-determining steps at different temperatures for the oxidations of thiocarbonohydrazide and its metal complex and hydrazone, by chloramine-B in aqueous perchoric acid and dichloramine-B in watermethanol (1:1, v/v).

	Chloramine-B oxidations			Dichloramine-B oxidation			
T/K	$K_1/dm^3$ mol <sup>-1</sup>	$k_2/10^{-3}$ s <sup>-1</sup>	$k_3/10^{-2} \text{ dm}^3$ mol <sup>-1</sup> s <sup>-1</sup>	$K_1/dm^3$ mol <sup>-1</sup>	$k_2/10^{-3}$ s <sup>-1</sup>	$k_3/10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	
Thioca	rbonohyd	razide					
283 288 293 298	52.5 30.7 26.9 10.6	2.4 4.5 6.3	2.7 4.7 8.8 15.6	19.4 15.4 16.7 23.3	2.8 3.2 4.1 5.0	3.4 4.6 4.8 7.7	
Metal	complex						
288 293 298	34.2 30.1 22.1	6.3 8.3 14.2	12.5 18.3 21.8	9.1 11.4 14.9	7.1 8.3 10.0	6.0 9.2 14.7	
Hydra	zone						
288 293 298	30.1 41.3 38.6	7.1 8.3 12.5	14.7 20.0 26.0	32.9 35.2 41.5	5.09 6.3 8.4	7.4 10.8 14.0	

In solutions of the substrate (S) in acid the following protonation equilibrium also exists.

### $S + H^+ \rightleftharpoons SH^+$

Under strongly acidic conditions most of the substrate exists in the protonated form.

Mechanism of Oxidations.—The kinetic results (first order in [oxidant], fractional order in [substrate], and zero order in  $[H^+]$ ) together with the lack of influence on the rate of oxidation of either added benzenesulphonamide or increase in ionic strength may be explained by either a Michaelis-Menten type mechanism (Scheme 3) or a two-pathway mechanism (Scheme 4).

PhSO<sub>2</sub>NHCl<sup>a</sup> + S 
$$\xrightarrow{K_1}$$
 Complex (X) (fast)

$$X \xrightarrow{k_2} S' + PhSO_2NH_2$$
 (slow)

$$S' + PhSO_2NHCl \longrightarrow products$$
 (fast)

Scheme 3. " Similarly for PhSO<sub>2</sub>NCl<sub>2</sub>.

or

Based on Scheme 3 the following rate laws were deduced.

$$-\frac{d[\text{oxidant}]}{dt} = \frac{K_1 k_2 [\text{oxidant}][S]}{1 + K_1 [S]}$$
(1)

*i.e.* 
$$k_{obs} = \frac{K_1 k_2 [S]}{1 + K_1 [S]}$$
 (2)

$$\frac{1}{k_{\rm obs}} = \frac{1}{K_1 k_2 [S]} + \frac{1}{k_2}$$
(3)

The plots of  $1/k_{obs}$  versus 1/[S] were reasonably linear in all cases in accordance with equation (3). From the slopes and intercepts of the plots, the constants  $k_2$  and  $K_1$  were calculated. Further, the substrate concentration was varied at different temperatures (283–298 K) and the constants  $k_2$  and K, were computed at each temperature (Table 2). The values of  $k_2$  were

used to calculate the activation parameters from the Arrhenius plots.

The two-pathway mechanism and the related rate laws are as follows:

Path 1 PhSO<sub>2</sub>NHCl<sup>*a*</sup> + S $\xrightarrow{k_3}$ S' + PhSO<sub>2</sub>NH<sub>2</sub> (slow)

$$S' + PhSO_2NHCl \longrightarrow products$$
 (fast)

Path 2 PhSO<sub>2</sub>NHCl + H<sub>2</sub>O 
$$\stackrel{K_4}{\longleftrightarrow}$$
 Intermediate (Y) (fast)

$$Y \xrightarrow{\kappa_3} HOCl + PhSO_2NH_2$$
 (slow)

$$S + HOCI \longrightarrow S' + H_2O$$
 (fast)

$$S' + HOCl \longrightarrow products$$
 (fast)

Scheme 4. " Similarly for PhSONCl2.

i.e.

The combined rate law [equation (4)] is in accordance with Scheme 3.

$$-\frac{d[\text{oxidant}]}{dt} = k_3[\text{oxidant}][S] + \frac{K_4k_5[\text{oxidant}][H_2O]}{1 + K_4[H_2O]}$$
(4)

$$k_{\rm obs} = k_3[S] + \frac{K_4 k_5[H_2O]}{1 + K_4[H_2O]}$$
(5)

or 
$$k_{obs} = k_3[S] + k'_5$$
, where  $k'_5 = \frac{K_4 k_5 [H_2 O]}{1 + K_4 [H_2 O]}$  (6)

The plots of  $k_{obs}$  versus [S] were also linear for all substrates with both oxidants (Figure). The slopes gave  $k_3$  (Table 3). The values of  $k_3$  were calculated at different temperatures (283–298 K) by varying the substrate concentration at each temperature (Table 3). The latter constants were also used to calculate the activation parameters from the Arrhenius plots (Table 2).

Although both the Michaelis–Menten type (Scheme 3) and the two-pathway mechanism (Scheme 4) explain the observed results for the oxidation of thiocarbonohydrazide in the free and metal-bound states and in its hydrazone, by either chloramine-B or dichloramine-B, the latter seems to be preferred, since the direct plots give relatively better correlations (Figure).







Detailed mechanisms of the oxidation of thiocarbonohydrazide and its hydrazones by  $PhSO_2NHCl$  are shown in Schemes 5 and 6; the mechanisms of oxidations by  $PhSO_2$ - $NCl_2$  and HOCl are similar.

The effects of solvent composition on the rates of ion-ion, ion-dipolar molecule, and dipolar molecule-dipolar molecule reactions have been discussed by several authors.<sup>19-22</sup> For the limiting case of zero angle of approach between two dipoles or an ion-dipole system, Amis<sup>19</sup> has shown that a plot of log  $k_{obs}$ versus  $1/\varepsilon_r$ , gives a straight line with a negative slope for the reaction between a negative ion and a dipolar molecule or between two dipolar molecules. The present experimental observations *i.e.* decrease of rate with decrease in relative permittivity \*  $(\varepsilon_r)$  of the medium (by increasing the methanol composition of the medium, 0-40%, v/v in chloramine-B oxidations and 30-60%, v/v in dichloramine-B oxidations) are in agreement with dipolar molecule-dipolar molecule interactions and the reaction pathways proposed to account for the observed kinetic data. The plots of log  $k_{obs}$  versus  $1/\varepsilon_r$  or % methanol were also linear with negative slopes, for all the oxidations.

The constancy of the free energies of activation gives an indication of the operation of a similar mechanism in all cases. The formation of more ordered activated complexes is evident from the large negative values (with one or two exceptions) of the entropy of activation (Table 2).

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<sup>\*</sup> Formerly known as dielectric constant.